

The Absorption Spectrum and Fluorescence of Mercury Vapour.

By W. N. HARTLEY, D.Sc., F.R.S.

(Received June 16, 1905.)

Having undertaken the investigation of the absorption spectra of metals in a state of vapour, the first substance examined was mercury, and as the results are interesting I have deemed it advisable to make them a separate communication to the Society. F. P. le Roux describes the vapour of mercury as having a bluish colour,* and according to R. J. Strutt, it transmits a feeble steel-blue colour, but the absorption coefficient is small.†

Experimental.—The substance to be volatilised was contained in a flask of Heraeus' quartz-glass, with a side tube to the neck from which the metal may be distilled and condensed. To the side tube a water-jacket is fitted through which a constant stream of water may be passed if necessary. The rays from the condensed spark of a pair of lead-cadmium and tin-cadmium electrodes were passed through the flask and on to a cylindrical condensing lens of quartz which focussed the rays on to the slit of a quartz spectrograph.

The mercury to be used was first purified by distillation. The photographic plates used were various, such as "Rainbow Fast" Warwick plates, Lumière isochromatic, yellow-green sensitive, and Cadett and Neall's "Lightning Spectrum" plates. The mercury vapour in the flask was at a pressure of 847 mm., the barometer standing at 763 mm., but the vapour was under a pressure of a column of 84 mm. of mercury above that of the atmosphere. The temperature was about 360° C., the b.p. at 760 mm. being 357°. The volume of the vapour was 31 c.c., and its weight was calculated to be 0.133 gramme. The thickness of the layer of vapour was 37 mm.

Several photographs were taken, and particular care was exercised so as to have both ends of the spectrum, as well as the central part, in accurate focus. The developer used was "imogen sulphite."

The Absorption Spectrum.—The whole rays were transmitted from the red to a point in the ultra-violet where there is a tin line at λ 2571.67. From there to λ 2526.8 there is a very sharply defined and intense absorption band, somewhat degraded on the side towards the red; beyond that the rays are transmitted with full intensity to a wave-length about 2000.

The Fluorescence.—When the mercury was boiling briskly the whole side of the flask nearest to the spark was lighted up with a green fluorescence;

* 'Comptes Rendus,' vol. 51, p. 171, 1860.

† 'Phil. Mag.' (6), vol. 4, p. 596, 1902, and vol. 6, p. 76, 1903.

this penetrated about one-third of the space within the flask, and lighted up the interior. The quartz-glass itself was not fluorescent in the slightest degree.

When all the liquid mercury had become converted into vapour, the temperature no doubt rose above that of the boiling mercury, the vapour was quiescent, and the fluorescence ceased. The interior of the flask was then quite dark. By shaking some of the condensed cold mercury down into the flask the fluorescence was resumed directly the liquid boiled again, but the dropping of cold mercury into the heated vapour caused condensation, and only after the flask had again become filled with the mercury vapour was the fluorescence fully displayed.

When the vapour was rising from the boiling globule of mercury after the cold metal had condensed all within the flask, the vapour could be seen by its fluorescence to undergo condensation in the upper part of the vessel and descend to the hotter space below.

It occurred to me that the actual fluorescence might be associated with oxidation of the vapour, and that it appeared only when such chemical action was taking place, but subsequent observations showed that this could not be the case, because the temperature was above that when oxidation could occur at the time when the fluorescence was most brilliant, and when it most completely filled the vessel, and also when the mercury vapour had expelled all the air. When the temperature rose above the boiling point of mercury and excess of liquid mercury and vapour had been expelled from the flask the fluorescence ceased.

This fact leads to the inference that the fluorescence occurs only between a lower and a higher limit of temperature. What these small differences really are I had no means of determining. Having established the fact that the property of selective absorption is possessed by small quantities of mercury vapour, it was resolved to ascertain whether the band showed itself in solutions of mercury compounds. As a rule the absorption spectra of compounds differ from those of the elements entering into their composition entirely, as in the case of the halogen compounds of the alkali metals; sometimes it is a question of degree, as in the case of the compounds of the rare earth metals, in which similar bands are observed in different salts of the same metal, but in different positions, which vary with the molecular weight of the salts; and there are, still further, other instances where the absorption bands of the solutions are distinctly the properties of the salts, as in the case of the chlorides, bromides, and iodides of cobalt. The salt chosen for examination, because it is the most definite and most soluble, was mercuric chloride. It was examined in cells of 40 mm. thick, diminishing to 1 mm. in thickness.

430 *Absorption Spectrum and Fluorescence of Mercury Vapour.*

The solution contained in the same volume ten times as much mercury as the vapour which filled the flask, or 1·8 gramme of mercuric chloride in 31 c.c. of water; more dilute solutions were examined containing 0·18 gramme and 0·018 gramme. No absorption band was visible on any of the spectra photographed, but there was a continuous absorption at the more refrangible end of the spectrum, which regularly diminished as the quantity of mercuric chloride in the solution decreased.

Further details are as follows :—

1·8 grammes of mercuric chloride in a cell 40 mm. thick transmitted all rays to λ 2702, in 1 mm. to λ 2572; 0·18 gramme in a cell 2 mm. thick transmitted all rays to λ 2265; and 0·018 gramme in similar circumstances transmitted very feebly to λ 2145.

The absorption band in the vapour of mercury belongs to the vapour, and is accompanied by strong fluorescence between a certain maximum and minimum of temperature lying very near to the boiling point.

In studying the fluorescence of solutions of organic compounds I have shown that it is necessary to use the ultra-violet rays and quartz apparatus,* as it was found that fluorescence was associated very generally with a powerful absorption of rays in the ultra-violet. It is a question still undecided whether the rays absorbed by mercury vapour as shown by the band I have measured, reappear with a lowered refrangibility as yellowish-green light in accordance with the law of Stokes.

The spectra were photographed with all due care by my assistant, Mr. Douglass Mellon, A.R.C.Sc.I.

* "Observations on the Origin of Colour and Fluorescence," 'Chem. Soc. Trans.,' vol. 63, pp. 245—256, 1893.